STATE OF CALIFORNIA

AIR RESOURCES BOARD

AIR MONITORING QUALITY ASSURANCE

VOLUME II

STANDARD OPERATING PROCEDURES

FOR

AIR QUALITY MONITORING

APPENDIX N

ACID DEPOSITION

MONITORING AND LABORATORY DIVISION

JANUARY 1986

TABLE OF CONTENTS

APPENDIX N
ACID DEPOSITION

APPENDIX N

ACID DEPOSITION

FIGURES

Page

STATE OF CALIFORNIA

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AIR QUALITY MONITORING

APPENDIX N.1

ACID DEPOSITION

FIELD SAMPLING AND ANALYSIS PROCEDURES

MONITORING AND LABORATORY DIVISION

JANUARY 1986

N.1.0 GENERAL INFORMATION

N.1.0.1 SYSTEM OPERATION

The precipitation sampler collects dry and wet precipitation in two 3.5 gallon plastic buckets. The dry precipitation bucket is shipped directly to the laboratory for analysis of the contents. The wet bucket contents are analyzed on site for precipitation volume, pH, and conductivity before the contents are shipped to the laboratory. At the laboratory, the bucket contents are analyzed for pH, conductivity, sodium, potassium, calcium, magnesium, ammonium, chloride, nitrate, and sulfate.

N.1.0.2 PHYSICAL DESCRIPTION

The precipitation sampler consists of an aluminum table, two 3.5 gallon plastic buckets, movable lid, thermistor heated rain sensor, and motor. During dry weather, the lid covers the wet bucket allowing dry precipitation to accumulate in the dry bucket. When water strikes the thermistor sensor, the motor starts, moving the cover from the wet to the dry bucket, allowing the rain to accumulate in the wet bucket. The wet bucket is exposed until the water evaporates from the thermistor sensor, causing the lid to move from the dry to the wet bucket.

N.1.0.3 CAUTIONS

1. Avoid contamination of the sample buckets at all times. Even a fingerprint on the inside wall of the bucket can cause erroneous analyses of the ions. It is recommended that personnel wear clean lab gloves when handling the buckets. In addition, do not exhale into a container, since the human breath contains ammonia.

N.1.1 SAMPLING PROCEDURE

N.1.1.1 SAMPLING FREQUENCY

The wet side bucket should be changed every Tuesday at 9:00 a.m. The dry side bucket is changed every eight weeks on Tuesday at 9:00 a.m. If it is raining, the changing of the buckets can be delayed up to 24 hours.

NOTE: In heavy snow conditions, the wet side bucket may fill up with snow. Replace the filled bucket with an empty bucket and allow the snow to thaw. Combine all of the thawed bucket samples for the week and analyze as the weekly sample.

NOTE: In heavy rain conditions, the bucket should be replaced before the bucket is completely full (approximately 9 inches of rain). Each bucket will be treated as a separate weekly sample and should be documented accordingly.

N.1.1.2 CHANGING SAMPLE BUCKETS

NOTE: Where physically possible, approach the collector and work from the downwind side to prevent windblown contaminants from entering the bucket.

1. To change the wet side sample bucket, short out the sensor by placing a coin across the sensor face.

2. Take a clean lid from its plastic bag and cap the old bucket, fastening the lid with masking tape.

3. Remove the capped bucket from the collector.

4. Remove the short from the sensor and clean the underside of the sampler roof with distilled or deionized water and/or wipe with a clean lab tissue.

5. Clean the sensor grid with distilled or deionized water. If necessary, use a toothbrush and detergent to remove the dirt film.

6. Inspect the dry side bucket for wet precipitation, which is evidence of possible

collector malfunction. If there is a malfunction, ascertain the source and report it on the report form (Figure N.1.1.1).

7. Label the new bucket dry side or wet side, time and date of installation, and site name and number.

8. Install bucket and remove the sensor short, if used.

N.1.1.3 RAIN GAUGE DATA

1. Change the rain gauge chart every Tuesday morning at 9:00 a.m.

2. Record the amount of daily precipitation in the field observation area of the Sample Report Form (Figures N.1.1.1 and N.1.1.2). Record the type of precipitation R = Rain, S = Snow, M = Mixture, and U = Unknown) for each day.

3. Add the daily amounts to obtain the week's total and record.

NOTE: Occasionally, meteorological conditions such as fog, dew, and mist can trigger frequent lid openings without collecting a measurable amount of precipitation. These conditions can be recognized from the event record on the rain gauge chart and are identified as cycling. When cycling occurs and there is no precipitation recorded for the week, rinse the wet bucket with 250 ml of distilled water. Treat the rinse as a normal sample by measuring pH and conductivity and shipping the remaining sample to the Central Laboratory. Identify the sample as a rinse on the report form (ADD-17).

N.1.1.4 FIELD SAMPLE PROCESSING

NOTE: Buckets sometimes contain foreign objects such as insects, feathers, bird droppings, etc. Never attempt to remove any contaminant from the bucket. Identify the contaminant on the sample report form.

1. Dry-Side Buckets

For dry-side buckets, seal the bucket, label, and ship to the Central Lab in the box in which the bucket was received. See Section N.1.2.3 for labeling and shipping information.

2. Wet-Side Buckets - No Precipitation

   a. Rinse the old bucket with 100 ml of distilled water. Measure the conductivity of the rinse water (see Section N.1.2.1) and record on the report form as rinse water conductivity.

      NOTE: On the first Tuesday of every month during the dry season, if there is no sample in the bucket, rinse the old bucket with 250 ml of distilled water. Measure the conductivity of this rinse and send the sample to the laboratory using the same procedures as for a sample. Be sure to enter "no precipitation" on the report form and return the form to the Central Laboratory.

   b. Enter "no precipitation" on the report form and return the form to the Central Laboratory.

   c. Clean the bucket, if necessary, (rinse water conductivity must be <2.0 μs/cm), dry, and store for future use (see Section N.2.0.1 for detailed cleaning instructions).

3. Wet-Side Bucket - With Precipitation

   a. Allow any snow or ice in the bucket to melt completely and attain room temperature (25°C $\pm$ 5°C) before proceeding.

   b. Wipe the outside of the bucket dry.

   c. If the bucket has more than 1000 ml (0.5 inches) of water, rinse the graduated cylinder with approximately 200 ml of sample. Note the exact amount of the rinse volume before discarding.

   d. Pour the total contents or the remaining contents into the graduated cylinder and record the total volume, including rinse volume, on the report form.

   e. If large capacity (10 kg) solution balance is available, determine the volume using the following procedure:

      1) With the balance level, adjust to zero (see manufacturer's instructions).

2) Before placing the new wet-side bucket into the collector, weigh the bucket, without the lid, to the nearest gram. Remember to avoid any contact with the bucket's inner surface. Record the weight of the empty bucket.

3) After sampling, tap the lid to knock off any water drops from the inside surface into the bucket. Wipe off water drops and any other material off the outside of the bucket.

4) After the balance has been zeroed, weigh bucket, without lid, to the nearest gram. Record weight.

5) Subtract the initial weight of the bucket from one sample weight to obtain the rain sample weight.

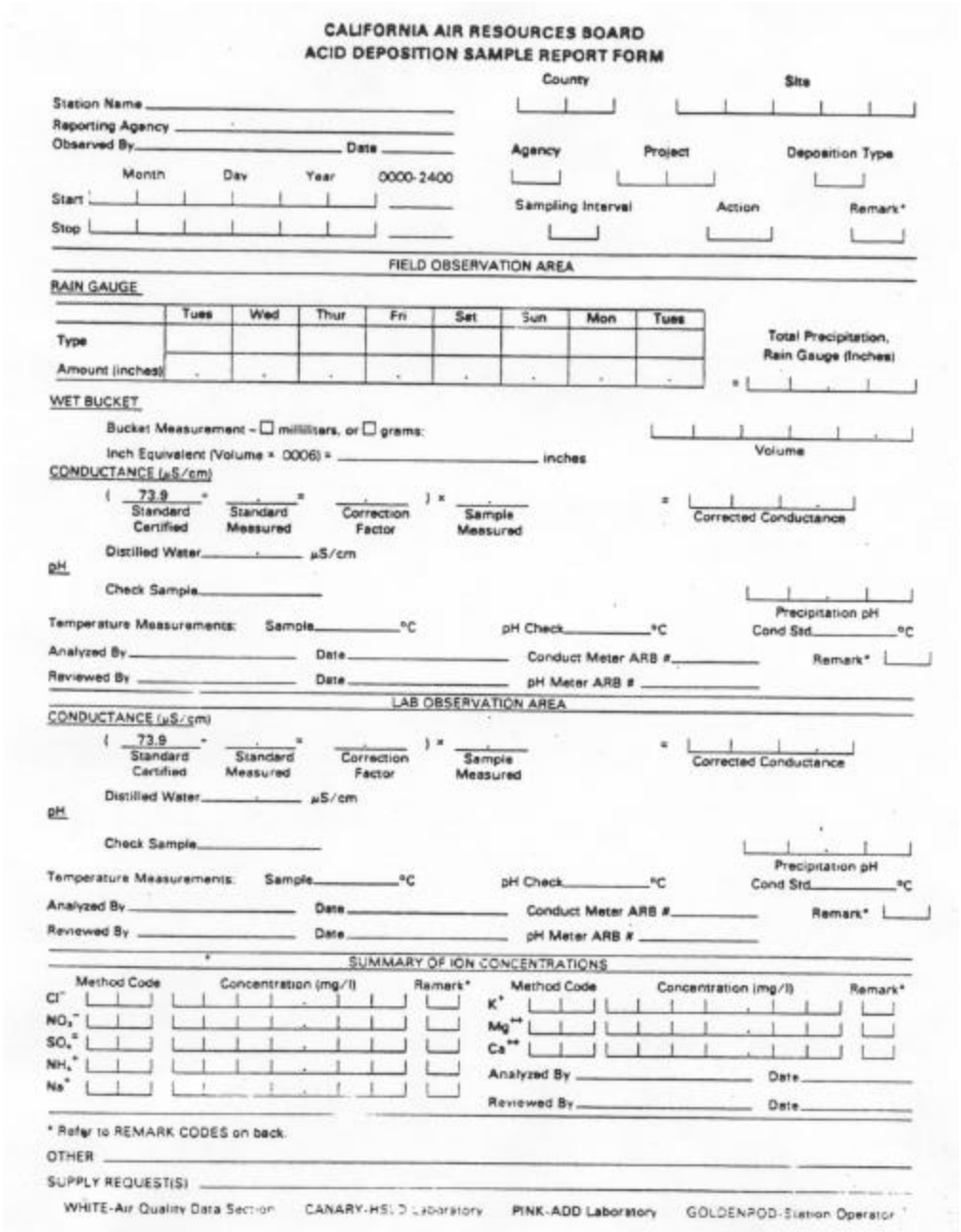
6) Record the sample weight in the volume "space" of the ADD-17 report form and check off the "bucket measurement" in grams.

7) Multiply the obtained volume by 0.0006 to calculate the "inch equivalent volume". Record the value on the ADD-17 report form.

f. If the total volume is less than 100 ml (150 ml for large cord cells), transfer the total volume to a clean polyethylene bottle, freeze the solution, and ship to the Central Lab as per Section N.1.2.3.

g. If the volume is >100 ml, save a minimum aliquot for your conductivity and pH measurements. Transfer approximately 100 ml to the clean 120 ml polyethylene bottle after rinsing the bottle with some of the sample. Allow 10 ml space in the bottle for expansion. Process the sample and ship to the Central Lab as per Section N.1.2.3.

h. Clean the bucket for future use (see Section N.2.0.1). Be sure the final rinse is less than 2 µs/cm.



CALIFORNIA AIR RESOURCES BOARD
ACID DEPOSITION SAMPLE REPORT FORM

Station Name _____ County ____ Site ____
Reporting Agency _____
Observed By _____ Date _____ Agency ____ Project ____ Deposition Type ____
Month Day Year 0000-2400
Start ____ Sampling Interval ____ Action ____ Remark* ____
Stop ____

FIELD OBSERVATION AREA

RAIN GAUGE

	Tues	Wed	Thur	Fri	Sat	Sun	Mon	Tues
Type								
Amount (inches)	.	.	.	.	.	.	.	.

Total Precipitation, Rain Gauge (Inches) = ____

WET BUCKET

Bucket Measurement – ☐ milliliters, or ☐ grams: ____ Volume
Inch Equivalent (Volume × 0006) = _____ inches

CONDUCTANCE (µS/cm)

(73.9 / Standard Certified - ____ / Standard Measured = ____ / Correction Factor) × ____ / Sample Measured = ____ Corrected Conductance

Distilled Water ____ µS/cm

pH

Check Sample _____ Precipitation pH ____

Temperature Measurements: Sample ____ °C pH Check ____ °C Cond Std ____ °C
Analyzed By _____ Date _____ Conduct Meter ARB # ____ Remark* ____
Reviewed By _____ Date _____ pH Meter ARB # _____

LAB OBSERVATION AREA

CONDUCTANCE (µS/cm)

(73.9 / Standard Certified - ____ / Standard Measured = ____ / Correction Factor) × ____ / Sample Measured = ____ Corrected Conductance

Distilled Water ____ µS/cm

pH

Check Sample _____ Precipitation pH ____

Temperature Measurements: Sample ____ °C pH Check ____ °C Cond Std ____ °C
Analyzed By _____ Date _____ Conduct Meter ARB # ____ Remark* ____
Reviewed By _____ Date _____ pH Meter ARB # _____

SUMMARY OF ION CONCENTRATIONS

	Method Code	Concentration (mg/l)	Remark*		Method Code	Concentration (mg/l)	Remark*
Cl^-				K^+			
NO_3^-				Mg^{++}			
$SO_4^=$				Ca^{++}			
NH_4^+				Analyzed By		Date	
Na^+				Reviewed By		Date	

* Refer to REMARK CODES on back.

OTHER _____

SUPPLY REQUEST(S) _____

WHITE-Air Quality Data Section CANARY-HSL Laboratory PINK-ADD Laboratory GOLDENROD-Station Operator

Figure N.1.1.1
Acid Deposition Report Form - Side A

INSTRUCTIONS FOR COMPLETING ACID DEPOSITION FORM

SAMPLE IDENTIFICATION:

A. **Upper Left Side.** Enter the ARB station name, agency responsible for station operation, the name of the station operator and the date that the data was recorded onto this form. Record the appropriate numbers for the date and time for starting and stopping the sampling.

B. **Upper Right Side.** Encode the ARB county code and site numbers, agency code, and project number. Record the depostion type (D = Dry, W = Wet) and sampling interval (W = Weekly, D = Eight Week, E = Event, Z = Nonstandard). The Action Code should be filled out with the following codes:

1 - If existing data is to be **Deleted**
2 - If new data is to be **Entered** on the bank
3 - If existing data is to be **Revised**

For data to be Deleted or Revised, complete the top and appropriate data section of the new data sheet and note the reason for the change in the OTHER Remarks section on the front of the form.

Note 1: The ARB assigns the ARB station name, county and site number, agency code and project number upon submittal of ARB site information forms by the reporting agency.

Note 2: Remark refers to the appropriate letter listed at the bottom of this page.

The body of the form consists of four parts, the Field Observation area, the Lab Observation area, the Summary of Ion Concentrations area, and Remarks area. The Field Observation area is to be filled out by the field operators. The Lab Observation area should be filled out by central lab personnel as should the Summary of Ion Concentrations area. The Remarks area should be filled out by all personnel as necessary.

If remarks are included, the appropriate code should be placed in the box on the front of the form for this purpose. Please avoid OTHER Remarks if possible. If supplies are needed, write requests in space provided at the bottom of the form.

FIELD OBSERVATION AREA:

RAIN GAUGE:

Precipitation Type and Amount. Record the type (R = Rain, S = Snow, M = Mixture, U = Unknown) and amount of precipitation in inches for every day of the week. Record the total amount of precipitation (in inches) for the sample, using rain gauge results only.

WET BUCKET

Bucket Measurement. Record the volume (mls) or weight (gm) of the precipitation sample in the space provided. Multiply the bucket measurement by a conversion factor of 0.0006 to determine the total inches of precipitation collected in the bucket, and record the results. If bucket volume is less than 100 ml ship entire sample to Central Laboratory.

CONDUCTANCE

Measure and record the conductance of distilled water. Measure and record the conductance of the standard, calculate the correction factor. Measure and record the conductance of the sample, multiply by the correction factor and record Corrected Conductance.

pH

Measure and record the pH of the check sample, and the precipitation sample.

The lab analyst should sign and enter the date of analysis, and enter the ARB instrument numbers of the pH meter and conductivity meter.

TEMPERATURE

Measure and record the temperature (°C) of the Sample, pH Check sample and the Conductance Standard.

LAB OBSERVATION AREA:

Follow the procedures outlined under Field Observation Area above.

SUMMARY OF ION CONCENTRATIONS.

Record the ARB method code (available from Air Quality Data Section), the concentration in the units indicated, and the remarks number as appropriate for each ion analyzed. For ion concentrations below the detection limit, record the detection limit preceded by "<". Record the analyst's signature and date of anaylsis.

Note 3: ARB method codes (see Code Table 4*)

REMARK CODES (Please try to confine remarks to the codes listed.)

A. Condensation from dew or fog in sample
B. Sampler malfunction
C. Sampler not in operation
D. Sample lost
E. Sample tainted
F. Sample not analyzed
Z. OTHER - Explain briefly on front of form
G. Insufficient sample volume
H. Sample from NADP site
I. Average of multiple analysis
J. Validity in question
K. Remeasured value
L. Rain gauge malfunction

*Tables and additional guidelines for coding air quality data can be found in the ARB publication "Air Monitoring Quality Assurance, Volume II" beginning with Chapter 2.0.2.1.

ADD-17 (Rev. 7-7-85)

Figure N.1.1.2
Acid Deposition Report Form - Side B

N.1.2 FIELD SAMPLE ANALYSES

NOTE: Before making any conductivity or pH measurements, allow all solutions, including standards and sample aliquots, to equilibrate to room temperature (25°C ± 5°C). Keep solution covered to prevent contamination.

N.1.2.1 CONDUCTIVITY MEASUREMENT

The following instructions are based upon the Yellow Springs Model 31. If your meter is different, consult the manufacturer's manual for instructions for zeroing and calibration and go to Step 2e.

1. Calibrate the conductivity meter as follows:

   a. Remove the 2-slotted head screws from the sides of the instrument and 4 similar screws from the bottom and then lift the instrument out of the case.

   b. Plug the instrument into a power source, set the Function Switch to the line position, and allow 5 minutes warm-up.

   c. Set the Range Switch to the x 1000 Ohms position and the Sensitivity control to its maximum setting (full clockwise).

   d. Connect the precision resistors called for below to the HI and LO Terminals of the instrument.

      NOTE: A high precision resistance box, such as a GR or ESI, is recommended for accurate calibration. If this is not available, resistors of 2K, 10K, 20K at ±.25 percent accuracy may be used for basic calibration.

   e. Adjust the Drive control for a dial indication of 2.0.

   f. Set 2000 ohms on the decade resistance.

   g. Adjust the LO control on the rear of the assembly until the shadow on the indicator tube is at maximum.

   h. Adjust the Drive control for a dial indication of 20.0.

   i. Set 20,000 ohms on the decade resistance.

j. Adjust the HI control on the rear of the assembly until the shadow on the indicator tube is at maximum.

k. Repeat steps f through j until the shadow is at maximum for both settings.

l. Set 10,000 ohms on the decade resistance.

m. Adjust the Drive control until the shadow on the indicator tube is at maximum; the dial should be reading within 2 minor division of 10.0.

n. If the dial reading is not correct, re-check calibration steps f through j.

2. Operation

a. Connect the instrument to power source.

b. Set the function switch to the "line" position and allow 5 minutes for warm-up.

c. Connect the conductivity cell leads to the HI and LO terminals.

d. Set the sensitivity control to minimum.

e. Rinse the cell, inside and out, three times with d/d water, discarding each rinse.

f. Shake off excess water on the cell, then immerse into distilled/deionized (d/d) water. Be sure to remove any air bubbles that may form in cell by moving cell up and down.

g. Rotate the range switch to the "XI µMHO" range (d/d water will have a conductance between 1 and 10 "µMHO/µ Siemans/cm).

h. Adjust drive control until the longest shadow has been reached.

NOTE: "Shadow" means the area of the electron ray tube which is not lit.

i. If necessary, adjust the sensitivity control until the edge of the shadow is short and well defined.

j. Read the value and record it in the "Distilled Water" space on the report form.

k. Remove the cell and rinse as in 2.e, shake and place into conductivity standard solution. Rotate the range switch to "X10 µMHO" since the standard is greater than 10 µMHO, but less than 100 µMHO.

l. Proceed as in paragraph 2.h through 2.i.

m. Read the value and then multiply by the value indicated on the range switch to get the value of the standard. Record the value in the space marked "standard measured" on the report form.

n. Remove the cell and rinse as in 2.e. Run through paragraph 2.h through 2.i for the rain sample. Depending on the sample's conductivity, the range switch may be on "X1 µMHO" or "X10 µMHO". Record the value in the space marked "standard measured" on the report form.

o. Calculate the "sample corrected" conductivity using a ratio technique as shown on the report form.

p. Set function switch to "off" and store the conductivity cell in d/d water until the next use.

N.1.2.2 pH MEASUREMENT

The following instructions are based upon a Fisher Accumet pH Meter Model 805. If your meter is different, consult the manufacturer's manual for instructions.

Precautions:

- If sample aliquot is used for both conductivity measurement and pH measurement, perform the conductivity measurement first.

- Store the pH check sample in the refrigerator. Transfer aliquot to two measurement containers, cover, and allow it to equilibrate to room temperature (25°C ± 5°C) before measuring first. Use one aliquot for temperature measurement; the other for pH.

- The sample, pH check sample, and pH buffer solutions should all be at room temperature (25°C ± 5°C) before measuring pH.

- For new electrodes, condition the electrode in distilled water or pH 7 buffer for at least eight hours at room temperature.

1. Power Up/Test: When the 805 is connected to an AC outlet a self-test sequence is performed. A series of numbers and messages is displayed. The numbers "187" and "13.00" are related to internal calibration check points. Normal messages will be test and ok. Should there be a malfunction, numerical values will be different and a second message will read Cal.

2. Slide the rubber sleeve off the hole on the upper part of the electrode. If the electrolyte solution is lower than one inch below the hole, top off the potassium chloride electrolyte solution to just below the hole after the measurements are made.

3. Rinse the electrode thoroughly using multiple rinses of distilled water (be sure to rinse the tip).

4. Gently blot the electrode tip dry with absorbent lab wipes (Kim wipes).

5. Immerse the electrode in an aliquot of the pH 7 buffer making sure the electrode does not contact the vessel bottom and that the electrode junction is covered. Swirl the solution gently and let stand three minutes for equilibrium.

6. To make a two point standardization Cal, press the "STBY/MEAS" key to place the 805 in measurement status.

   NOTE: The instrument's default mode is millivolt measurement.

7. Press the MODE key once to place into the pH measurement mode (pH and then a numeric value).

8. Press "TWO POINT CAL", display will read ("BOF" alternately with "ZERO")>

9. Key in the buffer value (7.00, decimal places optional).

10. Press the "ENTER" key to store the displayed data into the memory.

    Display: MV1 alternates with electrode potential. Check that MV value is constant, then press "ENTER" key to store data into memory. After MV value is entered a temperature value is requested.

11. Rinse the ASTM thermometer with distilled water, dry with an absorbent lab wipe and insert into the buffer solution. Read the temperature from the thermometer and key in the value ("SMP T" alternates with 0000); press the "ENTER" key to store the data into memory.

12. Repeat Steps 3 to 11 with the pH 4 buffer solution. The display of the meter will alternately show "BUF 2" and, "0".

13. With meter in pH measurement mode, repeat steps 3, 4 and 5 with the "check sample" and the precipitation sample. Record on readings record sheet. With the ASTM thermometer, confirm that the temperature of the "check sample" and the precipitation sample were within 0.5°C if the buffer samples. If the temperatures are not within 0.5°C, allow further equilibration time for the aliquot, and repeat the calibration and measurements.

    NOTE: The check sample measurement is a quality control check to assure that the pH measurement is a reasonably correct value.

14. Discard all used solutions.

15. Clean the electrode according to Step 3. Cover the electrolyte vent hole and store the electrode tip in pH 4 or pH 7 buffer. Change or add water as needed to the buffer solution to make up for evaporation.

N.1.2.3 SAMPLE SHIPMENT

If the field sample is shipped the same day as collected, freezing is not required. If shipment is delayed, then the sample shall be kept frozen (and unfiltered) until shipment to the lab.

1. Label the samples using a number 2 pencil (bucket or frozen wet sample, as applicable) with the following information:

    a. Station name and number

    b. Start and end sampling dates

    c. Sample type (wet or dry)

d. Sample volume or weight.

2. Ship the sealed bucket or sample bottles (frozen or ambient temp as applicable) to the Central Lab within 24 hours of collection via best method or as selected by the Central Lab. Use supplied shipping containers for shipment.

N.1.3 DOCUMENTATION

N.1.3.1 LOG BOOK

Record all problems and actions taken such as equipment changes, procedural changes, standard solution changes, electrode replacement, etc.

N.1.3.2 RAIN GAUGE CHARTS

1. Mark the charts with station name and number, dates, and notations for tests, etc.

2. Submit charts weekly to the Central Lab along with the acid deposition report form.

N.1.3.3 ACID DEPOSITION FORM

1. Complete the "Field Observation" and "Site Information" areas of the form, pressing hard enough to imprint all copies.

   NOTE: The remark code section of the acid deposition sample report from is used to record any unusual occurrences. Examples of unusual occurrences are equipment failure, sample contamination, power outage, dust storm, and a fire in the area. The importance of the information supplied in the remarks section cannot be over-emphasized. Careful observation and comments greatly aid in evaluating the validity of the sample.

2. Send three copies to the Central Lab and keep the fourth for the station's records.

STATE OF CALIFORNIA

AIR RESOURCES BOARD

AIR MONITORING QUALITY ASSURANCE

VOLUME II

STANDARD OPERATING PROCEDURES

FOR

AIR QUALITY MONITORING

APPENDIX N.2

ACID DEPOSITION SYSTEM MAINTENANCE

MONITORING AND LABORATORY DIVISION

JANUARY 1986

N.2.0 SYSTEM MAINTENANCE

N.2.0.1 PLASTICWARE CLEANING

1. If the vessel has only contacted clean rain water, proceed to Step 3.

2. Rinse the bucket with plenty of tap water. A clean sponge should be used if a dirty inner surface needs to be scrubbed. If a detergent must be used to remove a soiled part, use only a laboratory glassware cleaner such as Alconox.

3. Rinse thoroughly with distilled water at least three times.

4. Check the conductivity of the last rinse of every fifth bucket cleaned as per Section N.1.2.1. Record the conductivity in the log book. The conductivity should be less than 2.0 μs/cm.

5. Dry each vessel by placing it upside down on a clean surface in a manner that ventilation is sufficient for evaporation of water but the inner surface is protected from dust or other particulate.

6. When dry, place vessels in plastic bags for storage.

N.2.1 SAMPLER MAINTENANCE

The precipitation sensor should be tested weekly immediately after installing a new rain gauge chart. Place one drop of water on the sensor grip. The lid should then expose the wet side container and the event recorder should indicate the sampler has opened. After several minutes the top should return to cover the wet side container and the event recorder should indicate that the sampler has closed. Refer to the central lab personnel for information on replacing any of the component parts.

1. Winter operation

    a. Remove buildup of snow or ice on the sampler lid and sensor grid after a snow event.

    b. If necessary, encase the lid in plastic sheeting to prevent the arms from freezing to the table.

    c. If necessary, request and then attach a peaked roof to the lid to prevent buildup of snow. Once installed, the peaked roof should remain on the sampler year round.

N.2.2 RAIN GAUGE MAINTENANCE

1. Add antifreeze to the rain gauge pail if required. See manufacturer's manual for details.